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Trace Elements in a Columbia River Food Web

Abstract

The concentrations of several trace elements were measured by neutron activation analysis in caddisfly larvae and whitefish from the Columbia River. These concentrations were compared with previously measured levels in water and phytoplankton to examine trophic level relationships.

Concentrations of the majority of trace elements (Ag, Co, Cr, Cs, Fe, Na, Sb, Sc, and Zn) decreased through the food web. Potassium was the only element which increased in concentration, and four elements (Br, Hg, Rb, and Se) remained relatively constant. It was not possible to make generalizations, either seasonally or within tissues, concerning trace element concentrations in whitefish flesh, liver, and kidney. Comparison of these data with other published information reveals the complexity of food web relationships and the difficulty in extrapolation of data.

Introduction

Many data have recently been published concerning trace element analyses of a variety of environmental samples (e.g., Lucas *et al.*, 1970; Merlini *et al.*, 1969; and others). Few, however, have appeared concerning levels of trace elements in aquatic food webs—in particular, attempts to interpret the passage of trace elements through trophic levels. Mathis and Cummings (1973) presented data on selected metals in components of the Illinois River ecosystem, and Cushing and Rancitelli (1972) reported trace element analyses of Columbia River water and phytoplankton. Elwood *et al.* (1976) published data on trace elements in crane fly larvae (*Tipula* spp.), their gut contents and food (detritus), and interpretation of what they term the "trophic-transfer factor" (TTF) of various elements. Nomminga and Wilhm (1977) reported concentrations of various trace metals in water, sediments, and chironomid larvae.

As an extension of earlier work (Cushing and Rancitelli, 1972), I now quantify concentrations of the same elements reported previously from Columbia River water and phytoplankton in two higher trophic levels, namely the filter-feeding caddisfly larvae (Hydropsychidae) that ingest filtered phytoplankton, and whitefish *(Prosopium williamsoni)* that feed on caddisfly larvae by picking them from rocks or taking them as drifting organisms dislodged by the current. Combination of these data sets provides insight into the passage of various elements in the water→phytoplankton→caddisfly larvae→whitefish food web. Data are also presented on the distribution of various elements in whitefish flesh, kidney, and liver.

Methods and Materials

As described more fully by Cushing and Rancitelli (1972), attempts were made in 1970 and 1971 to collect the caddisfly larvae and whitefish samples at "ecologically significant" times of the year. These represented times of relatively long, stable environmental conditions (winter, summer) or periods of relatively rapidly changing conditions (spring and fall phytoplankton bloom periods, summer high water). Unfortunately, the schedule was adversely affected by unusual water conditions in 1971. Abnormally high water levels allowed sampling of caddisfly larvae only once, and whitefish were unobtainable in June and August.

All samples were collected from the Columbia River within the Hanford Reservation, but upstream from all effluents associated with the reactors. It is not known to what extent whitefish may have been subjected to plant effluents, but it is known that they may seasonally move several kilometers upstream (Cushing and Watson, 1966). The sampling station was located at River km 616, about 2 km above and across the river from the furthest upstream operating reactor.

Caddisfly larvae were collected by handpicking organisms from rocks. Larvae were frozen immediately with dry ice and kept frozen until neutron activated prior to analysis. Caddisfly larvae were analyzed with gut contents included since we were interested in the total element transfer to the whitefish, not just that included in the larval tissues or adsorbed to the organism (see Elwood *et al.* [1976] for further details on this aspect). Whitefish were collected in the same vicinity by angling and also were frozen until neutron activated. Analyses were performed on composite samples of whitefish flesh from six to eight fish, and on flesh, liver, and kidney of an individual fish from each of the four samplings.

Concentrations were determined by neutron activation analysis. The basic procedures for irradiation and subsequent separation and gamma spectroscopy were described by Rancitelli and Tanner (1969). Elements analyzed in both caddisfly larvae and whitefish were Ag, As, Au, Br, Co, Cr, Cs, Fe, Hg, K, Na, Rb, Sb, Sc, Se, and Zn. In addition, Eu, Hf, La, Sn, Ta, Tb, and Th were measured in caddisfly larvae.

Results and Discussion

Table 1 presents the elemental concentrations in caddisfly larvae and whitefish flesh on 16 November 1970, together with similar data from water and phytoplankton collected at about the same date two years earlier. Based on these results, K is the only element increasing in concentration through the food web from phytoplankton to whitefish flesh. Nine elements, occurring in all three trophic levels (Ag, Co, Cr, Cs, Fe, Na, Sb, Sc, and Zn), decreased in concentration, some more significantly than others; e.g., Ag as compared to Na. Levels of Br, Hg, Rb, and Se remained relatively constant. Seven elements were detected in caddisfly larvae only; two in water, caddisfly larvae, and whitefish only; and three in water only (Table 1).

The above comparison involves only concentrations of the elements in the flesh of whitefish; but varying levels of several elements were found in other tissues of the fish. Table 2 shows concentrations of 17 elements in the flesh, liver, and kidney of a single whitefish from each of the four sampling trips. In essence, there are two "fall" samples (16 November 1970 and 14 December 1971), one winter sample (18 February 1971), and one spring sample (15 April 1971). Sample collection by angling was unsuccessful in mid-summer.

Examination of these data shows that generalizations cannot be made either seasonally within a tissue or among the three tissues. For instance, Cs and Rb are remarkably constant both seasonally and among tissues, but Fe reflects a two order of magnitude difference among the tissues. Several elements have unusually high or low concentrations in a particular tissue on one sampling date; e.g., Sc in kidney, Zn in flesh. How much variation is attributable to true seasonal differences or to individual variation is difficult to ascertain, since only the values for flesh can be compared with composited samples from several fish taken at the same time. The composited values are shown in parentheses in Table 2. Agreement between composited and individual samples is good. It is not surprising to find inconsistencies when comparing such values considering the many variables involved—for example, age, previous exposure to effluents, etc.

TABLE 1. Elemental concentrations in Columbia River water, phytoplankton, caddisfly larvae, and whitefish flesh.

Element	ppb Water (11/14/68)	Phytoplankton (11/14/68)	ppm dry weight Caddisfly larvae (11/16/70)	Whitefish flesh (11/16/70)
Ag	0.50	0.93	0.039	<0.0015
As	2.5		0.0034	<0.82
Au	0.03		<0.016	<0.0057
Br	5.6	17.7	12.0	9.85
Co	0.02	9.11	0.87	0.022
Cr	0.40	22.8	1.8	<0.11
Cs	0.35	2.11	0.22	0.08
Cu	2.6			
Eu			0.056	
Fe	13.0	19200	2000	17.0
Hf			0.41	
Hg	<0.1	0.56	<1.0	0.405
K	1190	10700	12600	21000
La			1.6	
Mn	2.8			
Na	2200	8000	3900	1650
Rb	3.5	69.0	18.0	17.0
Sb	0.24	0.79	0.11	0.004
Sc	0.002	5.98	0.50	0.0003
Se	0.2	1.77	1.2	1.25
Sn			<12.0	
Ta			0.068	
Tb			0.066	
U	0.7			
Zn	8.0	1310	260	13.0

Comparison of these data with other studies is at best tenuous because of the varying analytical techniques, environmental conditions, sample handling, food, species, and so forth. The following discussion attempts to place the present data into some perspective.

Table 3 presents data on elemental composition of caddisfly larvae and a fish, the red-sided shiner *(Richardsonius balteatus)*, from the studies of Davis *et al.* (1958) in the Columbia River and this study. Values for Cr, Fe, and perhaps Co are similar for caddisfly larvae; however, our value for Zn is at least two orders of magnitude higher. Similar values for Cr and higher concentrations of Fe and Zn occur in the whitefish.

Mathis and Cummings (1973) reported analytical values for various elements in the flesh of five carnivorous fish species and five omnivorous fish species from the Illinois River near Peoria, Illinois. Although no whitefish were collected, the mean values for each of the two groups are compared with our data in Table 4 for three elements measured in common (see Mathis and Cummings [1973] for individual

TABLE 2. Elemental analyses of flesh, liver, and kidney from individual whitefish; values for composited flesh samples shown in parentheses.

	Flesh				Liver				Kidney			
Element	11-16-70	2-18-71	4-15-71	12-14-71	11-16-70	2-18-71	4-15-71	12-14-71	11-16-70	2-18-71	4-15-71	12-14-71
Ag[a]	5.1	<1.0		<1.0	110.2	28.0	240.0	160.0	91.0	12.0		53.0
	(<1.5)	(<1.3)		(<1.0)								
Au[a]	<5.8	<4.7			<12.0	<4.3			<21.0	<14.0		
	(<5.7)	(<6.6)										
Co[a]	22	35	32	17	200	420	200	220	1700	1700	640	880
	(22)	(24)	(33)	(67)								
Cr[a]	<240	<97	380	740	520	<100	<200	860	5200	430	780	12000
	(<110)	(135)	(170)	(<190)								
Cs[a]	90	53	98	61	49	47	44	59	46	27	44	68
	(80)	(59)	(75)	(51)								
Sb[a]	4.4	0.65	6.4	2.9	6.1	12.0	8.5	28.0	32.0	18.0	480	57.0
	(3.6)	(<.80)	(8.2)	(2.2)								
Sc[a]	<0.05	<0.05	<0.05	0.2	0.31	0.23	0.39	1.6	5.8	2.8	4.0	19.0
	(0.26)	(<0.05)	(0.16)	(0.2)								
As[b]	<1.3	0.61	1.4	0.94	<2.0	1.9	<4.0		1.8	<2.6	4.0	
	(<0.82)	(<0.86)	1.6	(<1.0)								
Br[b]	8.2	9.0	31.0	19.0	38.0	44.0	53.0	57.0	52.0	49.0	53.0	65.0
	(9.9)	(9.0)	(23.0)	(22.0)								
Cd[b]					10				104		5.3	
Fe[b]	17	23	38	17	230	750	150	32.0	690	1400	760	1300
	(17)	(18)	(33)	(24)								
Hg[b]	0.53	0.29	0.82	0.72	3.8	0.85	0.58	6.7	29.0	4.1	2.6	76.0
	(0.41)	(0.28)	(0.71)	(0.45)								
K[b]	22700	17800	19000	19100	19200	12700	13700	15200	15900	9900	19200	21700
	(21000)	(18200)	(19800)	(17600)								
Na[b]	1400	1200	5800	3000	3600	3800	5400	7200	4800	3700	5900	6700
	(1650)	(1200)	(3300)	(3500)								
Rb[b]	16	11	24	20	24	16	17	20	15	12	19	21
	(17)	(14)	(24)	(13)								
Se[b]	1.3	1.0	1.2	1.2	8.2	11.0	3.5	7.1	28.0	20.0	8.5	39.0
	(1.3)	(1.2)	(2.1)	(1.3)								
Zn[b]	13	11	42	19	91	84	140	260	120	57	97	89
	(13)	(11)	(26)	(24)								

[a]ppb dry wt.

[b]ppm dry wt.

species data). Zinc values are similar, but concentrations of Cr and Co are an order of magnitude less in Columbia River whitefish. The Illinois River receives considerably more domestic and industrial wastes than does the Columbia as reflected in the water concentrations shown in Table 4. Although this fact may partially explain the higher Cr and Co values in the Illinois River, it does not explain the similar Zn values. Since none of the data reported by Mathis and Cummings (1973) were from whitefish, the varying physiological demands among the species undoubtedly influences the levels found.

Table 5 presents comparative data for liver concentrations of two species of lentic whitefish (data averaged) from Lakes Michigan and Superior (Lucas *et al.*, 1970) and this study. Comparison shows values to be similar for Co and Zn, but considerably higher for As, Br, and Cd in Columbia River whitefish. No information is given for levels of these elements in the food of the Great Lakes fishes.

Comparison of trophic level changes is complex and certainly not straightforward (Enk and Mathis, 1977). The majority of elements measured in phytoplankton, caddisfly larvae, and whitefish flesh from the Columbia River decreased in concentration in this food chain. Conversion of data given by Mathis and Cummings (1973) to dry weights reveals that Cu, Ni, Pb, Cr, and Zn concentrations increased from sediments

TABLE 3. Elemental concentrations in Columbia River fish and caddisfly larvae (ppm dry weight).

Element	Caddisfly larvae[a] Davis et al. (1958)	Caddisfly larvae[a] This study	Fish Davis et al.[b] (1958)	Fish This study[c]
Cr	2.04	1.8	0.20	0.152
Co	<0.52	0.87	<0.52	0.037
Fe	1534	2000	2.04	23.0
Zn	<5.11	260	<5.11	18.5

[a]Hydropsychidae
[b]Richardsonius balteatus (whole fish minus gut contents)
[c]Prosopium williamsoni (flesh)

TABLE 4. Elemental concentrations in Columbia River and Illinois River water (ppm) and fish (ppm wet wt.).

Element	Columbia River Water	Columbia River Fish	Illinois River Water	Illinois River Fish Carnivorous	Illinois River Fish Omnivorous
Cr	0.0004	0.03	0.021	0.12	0.22
Co	0.00002	0.01	0.003	0.10	0.10
Zn	0.008	4.20	0.031	3.49	5.02

TABLE 5. Elemental concentrations in whitefish livers (wet weight).

Element	Columbia River (Prosopium williamsoni)	Lake Michigan (Coregonus clupeaformis)	Lake Superior (C. clupeaformis + P. cylindraceaum
Co	59 ppb		47 ppb
As	500 ppb	21 ppb	6 ppb
Br	11 ppm		0.3 ppm
Cd	2.3 ppm	0.09 ppm	0.4 ppm
Zn	33 ppm		28 ppm

to oligochaetes and that Li, Co, and Cd were essentially unchanged. All elements decreased in concentration in carnivorous fish flesh, although specific food items are not mentioned. Rabe and Bauer (1977) found that trace metals generally decreased in concentration from sediments to chironomid larvae to yellow perch flesh. Namminga and Wilhm (1977) found that concentrations of Cu and Zn increased and Cr and Pb decreased from sediments to chironomid larvae which also ingest sediments. Dean (1974), conversely, found that tubificid worms did not accumulate ^{65}Zn, ^{51}Cr, ^{54}Mn, ^{46}Sc, ^{137}Cs, or ^{59}Fe from sediments, but did accumulate ^{51}Cr, ^{60}Co, and ^{65}Zn from water containing dissolved radionuclides. Sediments have been shown to act as "sinks" for many contaminants including trace metals (Enk and Mathis, 1977; Mathis and Kevern, 1975; Mathis *et al.*, 1977; Cushing, unpublished) and radionuclides (Brungs, 1967; Robertson *et al.*, 1973).

Elwood *et al.* (1976) studied the relationship between the gut contents (detritus) and body burdens of trace elements in crane fly larvae. Their data allow comparison of elemental concentrations between (1) crane fly larvae with and without gut contents, and (2) larvae with gut contents and detritus, and (3) larvae without gut contents and detritus. Differences occur in increases or decreases in concentration of certain elements, but the second case is analogous to the phytoplankton-caddisfly larvae analyses in this study. Comparison of their data with that of this study shows that roughly twenty-two elements increased in concentration, seven decreased, and one was essentially unchanged in the crane fly larvae. In caddisfly larvae, one element increased, nine decreased and four were unchanged. Elwood *et al.* (1976) further calculate a trophic-transfer factor (TTF) which is a ratio indicating whether there is food chain enrichment from detritus to crane fly larvae without gut contents. A preponderance of elements had TTFs less than unity, indicating a decrease between trophic levels. Recalculation of these data, using crane fly larvae with gut contents, reveals that three times as many

TABLE 6. Biomagnification factors, $\frac{\text{concentration in organism}}{\text{concentration in food}}$ (dry weight).

Element	Tipula[a] / Detritus	Oligochaete / Sediment	Chironomid / Sediment	Caddisfly / Phytoplankton
Ag				.04
Br	3.3			.7
Co	1.3	.9[b]		.1
Cr	.4	2.0[b]	.4[d]	.1
Cs	1.7			.1
Fe	1.7			.1
K	1.8			1.2
Mn	1.3	.3[c]		—
Na	344			.5
Rb	—			.3
Sb	—			.1
Sc	1.5			.1
Se	2.1			.7
Zn	2.9	1.7[b]	3.6[d], .1[e]	.2

[a]Calculated from Elwood et al. (1976) using Tipula spp. with gut contents.

[b]Calculated from Mathis and Cummings (1973) after converting oligochaete data to dry weight using a factor of 3.3279.

[c]Same as (b) above from Mathis et al. (1977).

[d]From Namminga and Wilhm (1977).

[e]From Rabe and Bauer (1977).

elements show higher concentrations in the crane fly larvae than in the detritus. This point further emphasizes the contribution which gut contents make to total element transfer in food webs. Comparison of absolute values revealed that elemental concentrations in the crane fly larvae and caddisfly larvae were remarkably similar on a dry weight basis, and that concentrations in phytoplankton were considerably higher than in the detritus. This finding partially explains the larger number of elements decreasing in the phytoplankton-caddisfly larvae link.

Table 6 gives selected biomagnification factors for elements for which comparable data are available. The most obvious difference is in the predominance of values >1, indicating biomagnification, in the data from Elwood *et al.* (1976) as compared to nearly all values of <1 in the data from the Columbia River. Potassium is the only element for which data are available from more than one study that exhibits the same response, a value >1. Chromium decreased and Zn increased at three of the four sites.

These data emphasize the complexity of food web relationships and indicate that extrapolation of data among organisms and sites should be made with caution. In Table 6, for instance, we are comparing biomagnification factors for invertebrates from their respective food bases, but it includes at least four different organisms and three distinctly different foods. Comparisons such as these, however, may be useful in identifying general trends in the dynamics of nutrient cycling.

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